

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 008 580 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

14.06.2000 Bulletin 2000/24

(51) Int. Cl.⁷: C07C 45/50, C07C 29/141

(21) Application number: 99124566.3

(22) Date of filing: 09.12.1999

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 10.12.1998 JP 35111598

(71) Applicant:

MITSUBISHI CHEMICAL CORPORATION
Chiyoda-ku, Tokyo 100-0005 (JP)

(72) Inventors:

• Takagi, Masatoshi,
c/o Mitsubishi Chemical Corp.
Yokohama-shi, Kanagawa (JP)• Urata, Hisao,
c/o Mitsubishi Chemical Corp.
Yokohama-shi, Kanagawa (JP)

(74) Representative:

ter Meer, Nicolaus, Dipl.-Chem., Dr.
TER MEER STEINMEISTER & PARTNER GbR,
Patentanwälte,
Mauerkircherstrasse 45
81679 München (DE)

(54) Process for preparing aldehydes and alcohols

(57) A process for preparing aldehydes which comprises reacting an olefinic unsaturated compound with hydrogen and carbon monoxide by hydroformylation reaction in the presence of a catalyst in a continuous multistage flow reactor, wherein the continuous multistage flow reactor contains n number ($n \geq 2$) of flow reactors, and the reaction is carried out in the presence of pressure sectional zones satisfying at least one of the following pressure conditions (1) to (3), provided that partial pressures of hydrogen and carbon monoxide in each reactor are illustrated as $(P_{H_2(1)}, P_{CO(1)})$, $(P_{H_2(2)}, P_{CO(2)})$, ... $(P_{H_2(n)}, P_{CO(n)})$ in order from the

upper stream from the reactor,

$$P_{CO(m-1)} < P_{CO(m)} \quad (1)$$

$$P_{H_2(m-1)} < P_{H_2(m)} \quad (2)$$

$$P_{CO(m-1)} + P_{H_2(m-1)} < P_{CO(m)} + P_{H_2(m)} \quad (3)$$

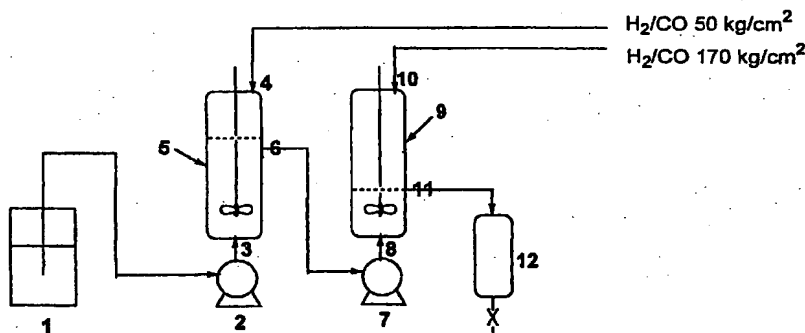
in which m is an integer in the range of $2 \leq m \leq n$.

FIG. 1

EP 1 008 580 A1

Description

[0001] The present invention relates to a process for preparing aldehydes and alcohols, and particularly relates to a hydroformylation reaction system to obtain aldehydes at a high activity and a high selectivity.

[0002] It is well known to hydroformylate an olefinic unsaturated compound with a H_2/CO mixed gas in the presence of a catalyst and it is also known to use a continuous multistage flow reactor as a method for industrially favorably conducting this reaction.

[0003] For example, JP-A-61-218546 discloses to use a two stage decouple reaction system wherein a gaseous distillate containing unreacted olefin, H_2 and CO remained after reaction in the first stage reactor is supplied as it is to the second stage reactor to carry out hydroformylation reaction, and also discloses to operate by using a separate catalyst solution-withdrawing step and a separate product-withdrawing step to each reactor. This reference discloses that a conversion of an olefin to an aldehyde is improved and also flexibility of the operation is improved, as effects of the decouple reaction system.

[0004] Also, JP-A-3-204831 discloses a method for hydroformylation of an olefin by using a specific combination of reaction systems having two different mixing properties, and discloses a method for obtaining an aldehyde at a high yield by preventing formation of by-products such as a low boiling point material, a high boiling point material and the like.

[0005] However, although these prior arts provide a method for obtaining an aldehyde at a high yield by raising an olefin conversion, there was no prior art providing a method satisfying both of a high olefin conversion and a high selectivity of a product, which are industrially important performances. Heretofore, it has been considered that a high olefin conversion and a high selectivity of a product are performances opposed to each other, and it has been technically difficult to provide a process satisfying both of the opposed two performances.

[0006] The present inventors have studied a process for hydroformylation of an olefinic unsaturated compound by using a continuous multistage reactor, and have noted that a pressure relation between each reactor has an influence on a reaction activity and a selectivity. As this result, the present inventors have discovered that a product can be obtained at a higher reaction rate and a higher selectivity by carrying out hydroformylation reaction by dividing into a plurality of pressure sections by using a multistage reactor, as compared with an operation under a single reaction pressure, and the present invention has been accomplished on the basis of this discovery.

[0007] That is, the essential feature of the present invention resides in a process for preparing aldehydes which comprises reacting an olefinic unsaturated compound with hydrogen and carbon monoxide by hydroformylation reaction in the presence of a catalyst in a continuous multistage flow reactor, wherein the continuous multistage flow reactor contains n number ($n \geq 2$) of flow reactors, and the reaction is carried out in the presence of pressure sectional zones satisfying at least one of the following pressure conditions (1) to (3), provided that partial pressures of hydrogen and carbon monoxide in each reactor are illustrated as ($P_{H_2}(1), P_{CO}(1)$), ($P_{H_2}(2), P_{CO}(2)$), ... ($P_{H_2}(n), P_{CO}(n)$) in order from the upper stream from the reactor,

$$P_{CO(m-1)} < P_{CO(m)} \quad (1)$$

$$P_{H_2(m-1)} < P_{H_2(m)} \quad (2)$$

$$P_{CO(m-1)} + P_{H_2(m-1)} < P_{CO(m)} + P_{H_2(m)} \quad (3)$$

in which m is an integer in the range of $2 \leq m \leq n$.

[0008] Hereinafter, the present invention is further described in more details.

[0009] The present invention provides a process for preparing aldehydes by hydroformylating an olefinic unsaturated compound with hydrogen and carbon monoxide in the presence of a catalyst in a continuous multistage flow reactor.

[0010] The continuous multistage flow reactor used in the present invention is a reactor obtained by connecting a plurality of reactors in series. Usually, the number (n) of reactors is from 2 to 10, preferably from 2 to 5, particularly preferably 2, but the number of reactors can be determined optionally depending on reaction conditions. The reactors used herein may be any type of reactors so long as mixing of gas-liquid can be satisfactorily carried out, and examples include a stirring tank type reactor, a plug flow type reactor and the like. Respective reactors in the continuous multistage reactor may be the same type, or plural types of reactors may be combined.

[0011] Operation conditions of the continuous multistage reactor used in the present invention vary substantially depending on a kind of an olefinic unsaturated compound used, but are generally as illustrated below. A reaction temperature is from 20 to 200°C, preferably from 50 to 160°C, more preferably from 100 to 150°C. The reaction temperature of each reactor may be the same or different. It is preferable that a total pressure of H_2/CO mixed gas used is in the range of from 10 to 300 kg/cm², preferably from 30 to 250 kg/cm², in all of reactors.

[0012] As mentioned above, the present invention employs a n number ($2 \leq n$) of continuous flow reactors, and is characterized by achieving a high olefin conversion, a high selectivity, e.g. a high n/i ratio and a high terminal formylation rate by controlling a hydrogen partial pressure, a carbon monoxide partial pressure or their total pressure.

[0013] Particularly, the reaction is carried out in the presence of pressure sectional zones satisfying at least one of the following pressure conditions (1) to (3), provided that partial pressures of hydrogen and carbon monoxide in each reactor are illustrated as $(P_{H_2(1)}, P_{CO(1)})$, $(P_{H_2(2)}, P_{CO(2)})$, ... $(P_{H_2(n)}, P_{CO(n)})$ in order from the upper stream from the reactor,

$$P_{CO(m-1)} < P_{CO(m)} \quad (1)$$

$$P_{H_2(m-1)} < P_{H_2(m)} \quad (2)$$

$$P_{CO(m-1)} + P_{H_2(m-1)} < P_{CO(m)} + P_{H_2(m)} \quad (3)$$

in which m is an integer in the range of $2 \leq m \leq n$.

[0014] In the present invention, at least two reactors connected in series in the continuous multistage flow reactor have only to satisfy the above conditions, and pressure conditions in other reactors are not restricted. Particularly, it is preferable to satisfy the condition of $m=2$ in any one of the formulae (1) to (3).

[0015] By providing pressure sectional zones satisfying at least any one of the above formulae (1) to (3), a selectivity (n/i ratio, terminal formylation rate or the like) is preferentially raised in a $(m-1)$ stage reactor having a relatively low pressure, and it is possible to raise a conversion of an olefinic compound in a m stage reactor having a relatively high pressure.

[0016] Also, more preferably, it is favorable to employ pressure sectional zones satisfying the following conditions.

$$P_{CO(m-1)} / P_{CO(m)} = 1.5-5$$

$$P_{H_2(m-1)} / P_{H_2(m)} = 2-5$$

$$(P_{CO(m-1)} + P_{H_2(m-1)}) / (P_{CO(m)} + P_{H_2(m)}) = 1.5-5$$

[0017] More particularly, when among hydrogen partial pressures of n number of reactors, the lowest value is A and the highest value is B , it is preferable to carry out the reaction in pressure sectional zones of $B/A = 1.2-10$, preferably 1.3-8, more preferably 1.5-5, or when among carbon monoxide partial pressures of n number of reactors, the lowest value is C and the highest value is D , it is preferable to carry out the reaction in pressure sectional zones $D/C = 1.8-10$, preferably 1.9-8, more preferably 2-5. Among them, it is more preferable to carry out the reaction under such conditions as satisfying both of B/A and D/C in the above-mentioned ranges, and more particularly, when among a total pressure of hydrogen and carbon monoxide in n number of reactors, the lowest value is E and the highest value is F , it is preferable to carry out the reaction in pressure sectional zones of $F/E = 1.1-10$, preferably 1.3-8, more preferably 1.5-5.

[0018] A H_2/CO ratio in a H_2/CO mixed gas used is not specially limited, but is usually $1/5-5/1$, preferably $1/3-3/1$, more preferably $1/2-2/1$. It is most preferable to use a mixed gas having a H_2/CO ratio of about $1/1$ which is industrially easily available. The "partial pressure" defined in the present invention means a partial pressure of a gas phase of a reactor in the case of a stirring tank type reactor, and means an average partial pressure of a partial pressure at the inlet and a partial pressure at the outlet of a reactor in the case of a reactor having a pressure distribution in the reactor such as a plug flow type reactor.

[0019] When carrying out the reaction, a reaction starting material of liquid phase is transferred from the upper reactor to the lower reactor, but with regard to a reaction starting material of gas phase, H_2/CO gas may be supplied independently to each reactor, and a gas containing H_2/CO gas may be withdrawn from a gas phase of one reactor and may be supplied to another reactor as a supplying gas.

[0020] In the reaction system of the present invention, there may be employed a stripping system which comprises continuously supplying an unsaturated compound and an oxo gas to a reaction zone having a liquid phase containing a rhodium complex catalyst and having the formed aldehyde together with an unreacted oxo gas withdrawn from the reaction zone or there may be employed a liquid cycling system which comprises continuously supplying a reaction solvent containing a catalyst, an unsaturated compound and an oxo gas to a reaction zone, continuously withdrawing a reaction product solution containing the formed aldehyde from the reaction zone, separating at least a part of the formed aldehyde, and recycling a reaction solvent containing a remaining catalyst to the reaction zone.

[0021] An average residence time in each reactor constituting the continuous multistage flow reactor is fixed so as to achieve an aimed reaction conversion under practical reaction conditions, and is usually from 1 minute to 10 hours, preferably from 10 minutes to 8 hours, more preferably from 30 minutes to 7 hours.

[0022] Depending on operation conditions of the reactor, an aldehyde product is further hydrogenated to produce an alcohol at the same time. Accordingly, when an aimed final product is an alcohol, a load of hydrogenation step at a later stage can be omitted or reduced. By employing the process of the present invention, it is possible to increase an amount of an alcohol produced together with an aldehyde, and an industrial merit is great in respect that a load of hydrogenation step at a later stage can be reduced.

[0023] An olefinic unsaturated compound used in the present invention is an unsaturated organic compound having at least one carbon-carbon double bond, some of which have a functional group and others of which have no functional group. Examples of having no functional group include C₃-C₁₂, preferably C₄-C₁₀, unsaturated compounds and their isomers, such as propene, butenes, butadienes, pentenes, pentadienes, hexenes, octenes, nonenes, decenes and the like. Also, examples of having a functional group include allyl alcohol, allyl ethers, acrolein, acrylates, butenals, butenic acid esters, pentalals, penteric acid esters, and the like. In the present invention, any of an internal olefin and a terminal olefin can be used, but an internal olefin is preferable in respect that an effect for improving a selectivity of a terminal isomerized product industrially demanded can be fully achieved. Also, it is preferable to employ a plurality of mixtures of these olefins, and it is particularly preferable to employ mixed octene obtained by dimerization of butene which is industrially easily available.

[0024] A reaction conversion of an olefinic unsaturated compound is usually 50-100%. Particularly, when the olefinic unsaturated compound is a mixture of at least two kinds of compounds, it is preferable to make a reaction conversion high, at least 75%, preferably at least 80%, more preferably at least 85%.

[0025] A catalyst used in the present invention may be any catalyst so long as it is effective for hydroformylation of an olefinic unsaturated compound. Examples of a metal component contained in the catalyst include Group 8 to Group 10 elements of the Periodic Table such as rhodium cobalt, ruthenium, palladium, platinum, iron and the like, and among them, rhodium or cobalt is preferable, and rhodium is most preferable.

[0026] When using rhodium as a catalyst component, 0 valent or cationic compounds of rhodium can be used, examples of which include Rh(NBD)(acac), Rh(COD)(acac), Rh(acac)₂, [Rh(COD)Cl]₂, [Rh(NBD)Cl]₂, Rh(CO)₂(acac), and rhodium carbonyl clusters such as Rh₄(CO)₁₂ and Rh₆(CO)₁₆.

[0027] It is preferable to employ a metal component in the form of a complex.

[0028] Examples of a usable ligand include a compound known in prior arts to be workable as a ligand to a metal used, such as monodentate and multidentate phosphines, phosphites, amines and the like, but it is not always necessary to use such a ligand.

[0029] More particular examples of a compound usable as a ligand include phosphines such as a trialkylphosphine and a triarylphosphine including triphenylphosphine, tritolylphosphine or the like.

[0030] Examples of phosphites include triarylphosphites, trialkylphosphites, alkylarylphosphites and the like, and optional organic phosphites among the above illustrated phosphites can be used. Also, polyphosphites such as a bisphosphite, a trisphosphite and the like, which have a plurality of these phosphite structures in a molecule, can be used.

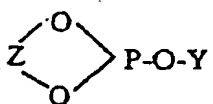
[0031] Among these phosphites, a monophosphite is classified into one having no cyclic structure containing a phosphorus atom and one having such a structure. The former one is expressed by the following formula (1).



[0032] In the above formula (1), R¹ to R³ are respectively independently a C₁-C₃₀ hydrocarbon group or a C₅-C₃₀ heteroaromatic hydrocarbon group, such as an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group or the like, and these groups may have a substituent bonded, which does not inhibit hydroformylation reaction. Examples of such a substituent include a halogen atom, a C₁-C₂₀ alkyl group, a cycloalkyl group, an aryl group, an alkoxy group, an alkylamino group, an acyl group, an acyloxy group, an alkoxycarbonyl group, and the like. Among organic phosphites expressed by formula (1), it is preferable that at least one of R¹ to R³ is a substituted aryl group.

[0033] Particularly preferable examples of an organic phosphite of the formula (1) include an organic phosphite, all of R¹ to R³ of which are substituted aryl groups, particularly a substituted aryl group having a C₁-C₅ hydrocarbon group as a substituent. Examples of such an organic phosphite include tris(2,4-di-t-butylphenyl)phosphite, tris(2-t-butyl-4-methylphenyl)phosphite, tris(2-t-butyl-4-methoxyphenyl)phosphite, tris(o-phenylphenyl)phosphite, tris(o-methylphenyl)phosphite, bis(3,6-di-t-butyl-2-naphthyl)(2,4-di-t-butylphenyl)phosphite, bis(3,6-di-t-butyl-2-naphthyl)(2-t-butylphenyl)phosphite, tris(3,6-di-t-butyl-2-naphthyl)phosphite, tris(3,6-di-t-amyl-2-naphthyl)phosphite, and the like.

[0034] Among monophosphites, one having a cyclic structure containing phosphorus atom is expressed by the following formula (2).



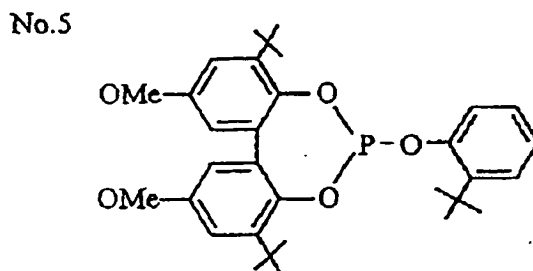
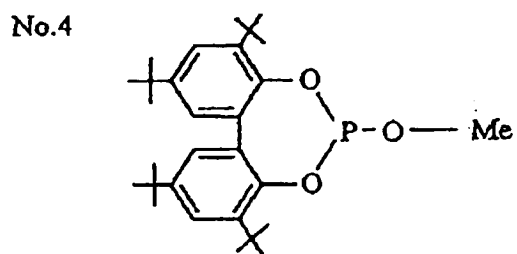
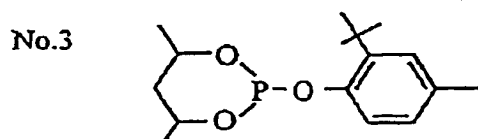
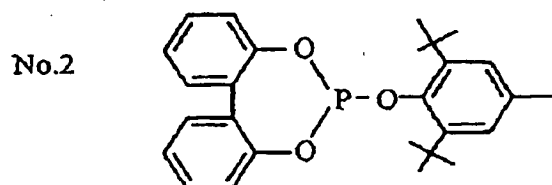
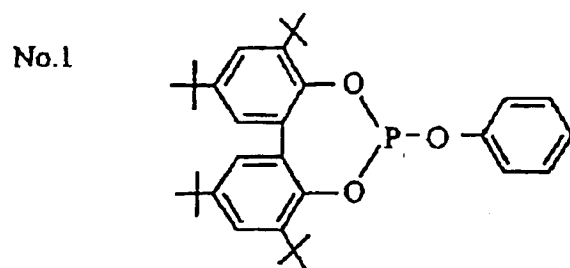
(2)

[0035] In the above formula, Z is a divalent hydrocarbon group which may contain a heteroatom in a carbon chain, and Y is a hydrocarbon group or a heteroaromatic hydrocarbon group, which may be substituted.

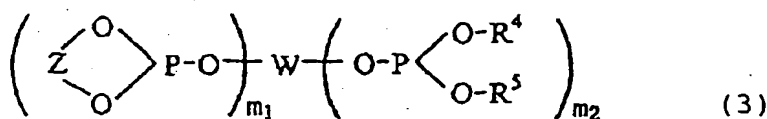
[0036] In the above formula (2), Y is preferably a substituted aryl group. Also, Z is preferably an alkylene group, an arylene group or a mixed group of the two, which may contain a heteroatom such as an oxygen, nitrogen or sulfur atom in a carbon chain. Examples of such a divalent hydrocarbon group include an alkylene group, an alkyleneoxyalkylene group, an alkyleneaminoalkylene group which may have an alkyl group bonded to a nitrogen atom, an alkyleneethioalkylene group, a cycloalkylene group, an arylene group, a biarylene group, an alkylenearylene group, an arylenealkylenearylene group, an aryleneoxyarylene group, an aryleneoxyalkylene group, an aryleneethioarylene group, an aryleneethioalkylene group, or an aryleneaminoarylene or aryleneaminoalkylene group which may have an alkyl group bonded to a nitrogen atom, and the like.

[0037] Some examples of the above-mentioned organic phosphite having a cycling structure containing a phosphorus atom are illustrated in the following Table 1.

Table 1



[0038] A polyphosphite having at least 2 phosphite structures in a molecule used as a ligand in the present invention is expressed by the following formula (3).



5
10 [0039] In the above formula, Z is the same as defined in with regard to the formula (2), and R⁴ and R⁵ are respectively independently a C₁-C₃₀ hydrocarbon group or a C₅-C₃₀ heteroaromatic hydrocarbon group, such as an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group, and the like, and these groups may have a substituent bonded, which does not inhibit hydroformylation reaction. Examples of such a substituent include a halogen atom, a C₁-C₂₀ alkyl group, a cycloalkyl group, an aryl group, an alkoxy group, an alkylamino group, an acyl group, an acyloxy group, an alkoxycarbonyl group, and the like.

15 [0040] W is a m-valent hydrocarbon group which may contain a hetero atom such as an oxygen, nitrogen or sulfur atom in a carbon chain. W may further have a substituent bonded. m₁ and m₂ are respectively a number of from 0 to 6, and m₁+m₂ is an integer of from 2 to 6. Also, when m₁ or m₂ is a number of at least 2, a plurality of Z, R⁴ and R⁵ may be respectively different.

20 [0041] Preferably, R⁴ and R⁵ are an aryl group which may be substituted. Examples of such an aryl group include a phenyl group, a 2-methylphenyl group, a 3-methylphenyl group, a 4-methylphenyl group, a 2,4-dimethylphenyl group, a 2,5-dimethylphenyl group, a 2,6-dimethylphenyl group, a 2-methoxyphenyl group, a 3-methoxyphenyl group, a 4-methoxyphenyl group, a 2,4-dimethoxyphenyl group, a 2,5-dimethoxyphenyl group, a 2,6-dimethoxyphenyl group, an α-naphthyl group, a 3-methyl-α-naphthyl group, a 3,5-dimethyl-α-naphthyl group, a β-naphthyl group, a 1-methyl-β-naphthyl group, a 3-methyl-β-naphthyl group, and the like.

25 [0042] Some examples of the polyphosphite of the formula (3) are illustrated in the following Table 2.

30

35

40

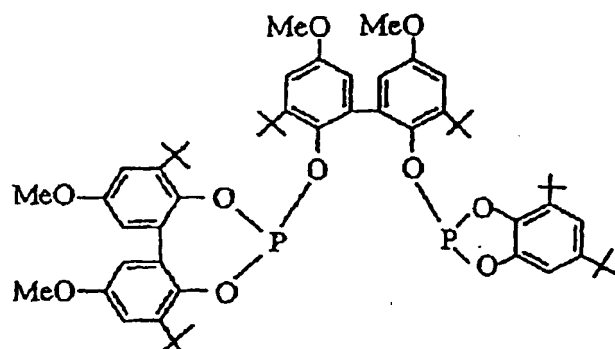
45

50

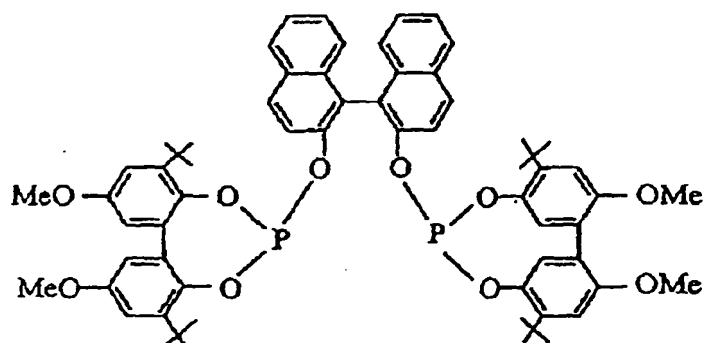
55

Table 2

No.1



No.2



No.3

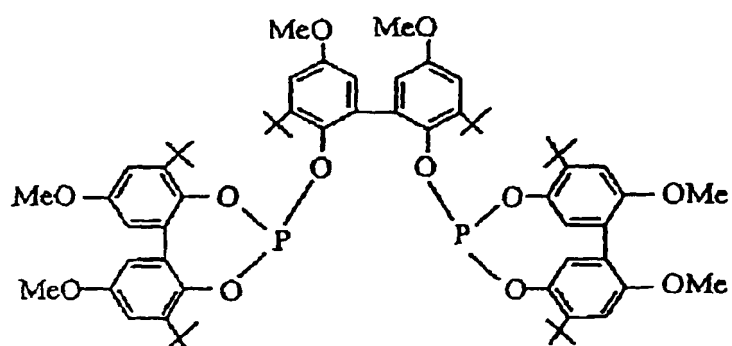
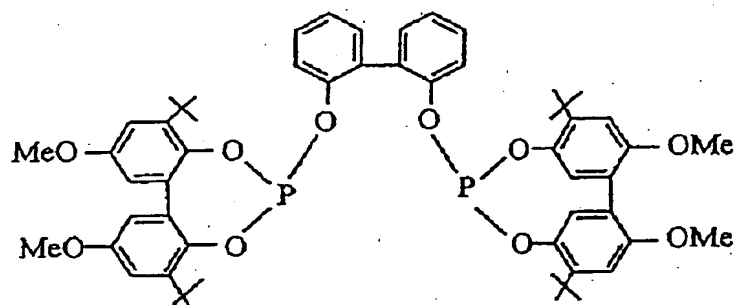
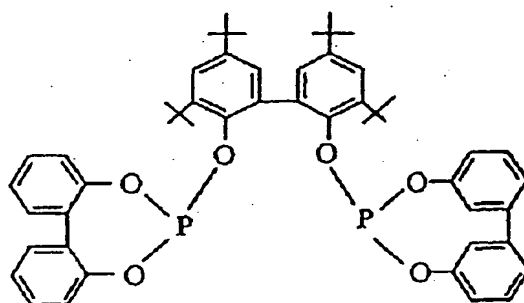


Table 2 (continued)

No.4



No.5



No.6

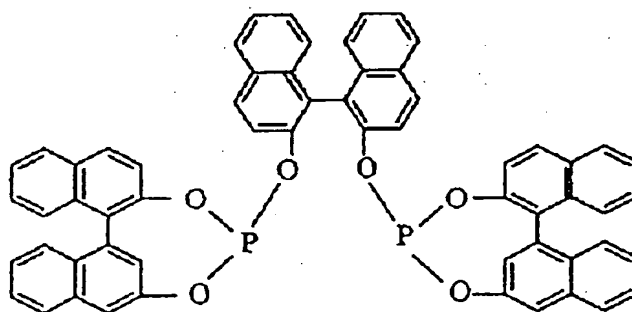
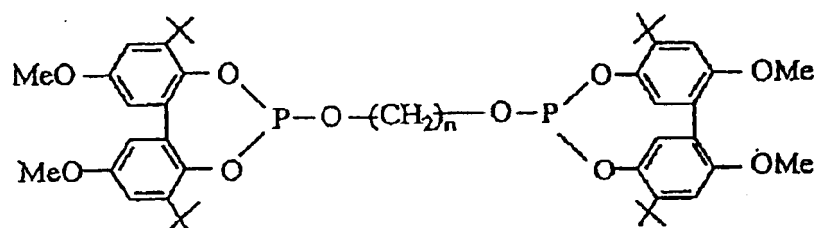
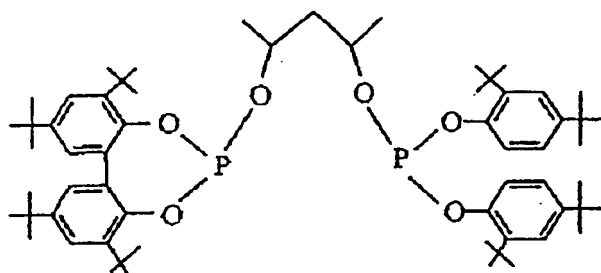


Table 2 (continued)

No.7



No.8



No.9

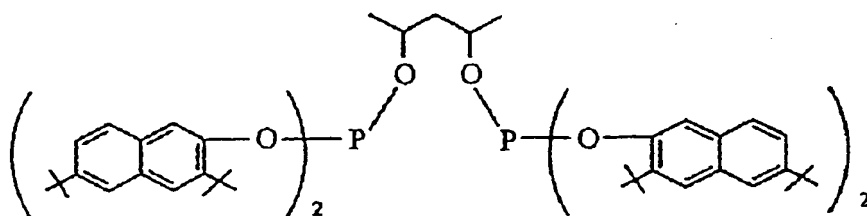
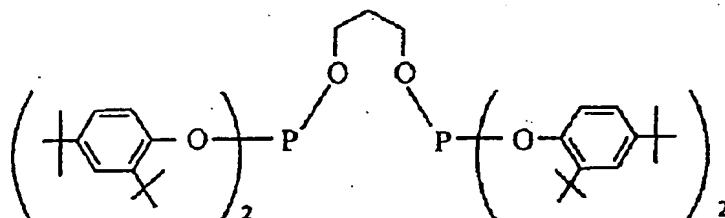
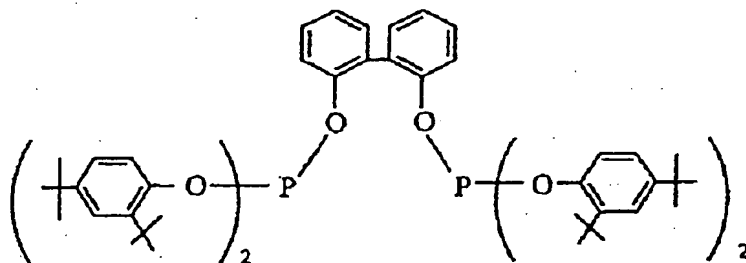


Table 2 (continued)

No.10



No.11



No.12

No.13

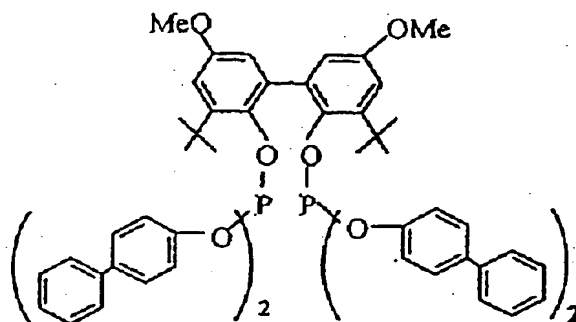
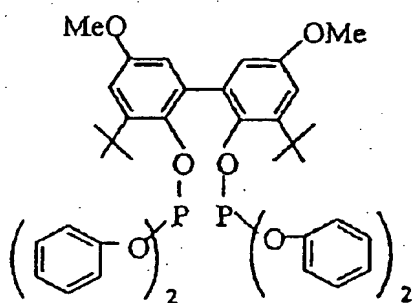
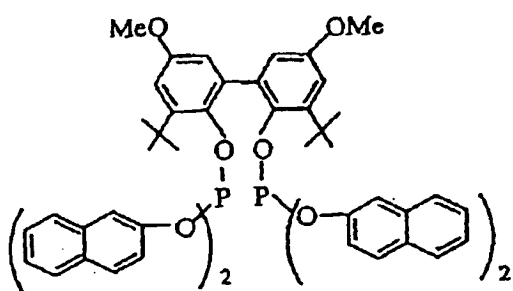
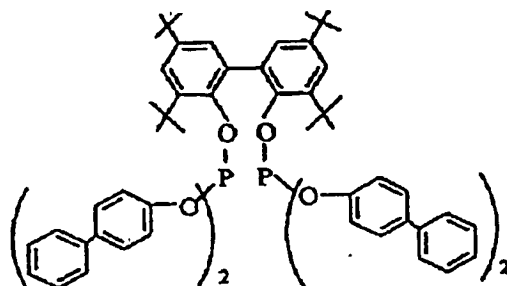


Table 2 (continued)

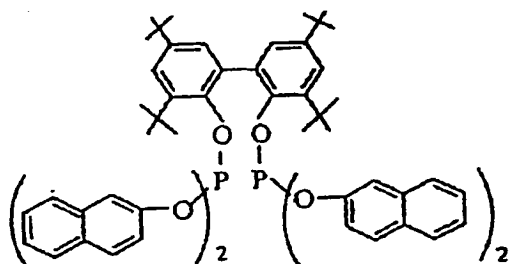
No.14



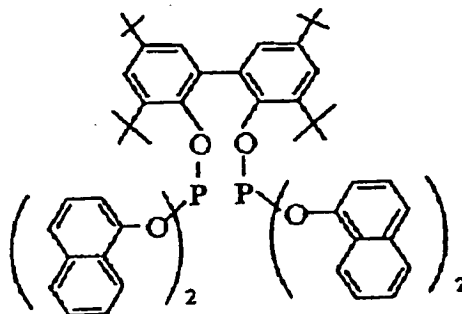
No.15



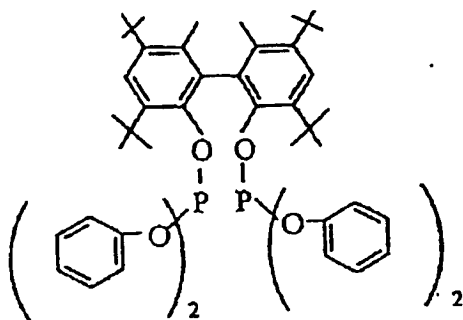
No.16



No.17



No.18



No.19

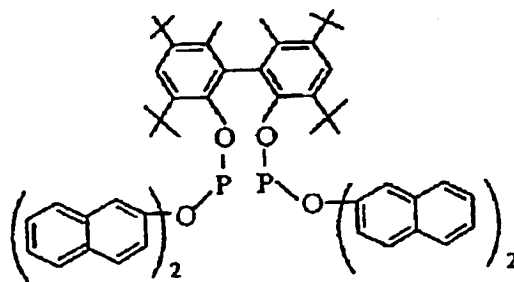
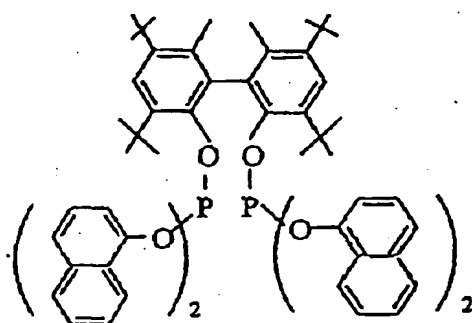
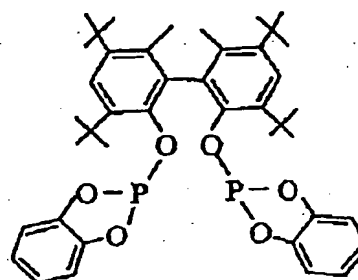


Table 2 (continued)

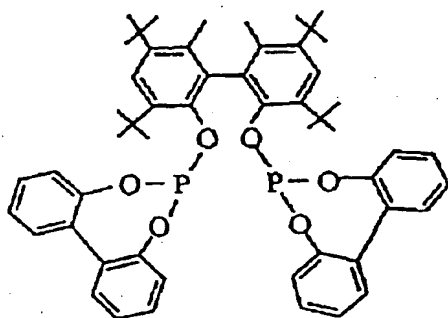
No.20



No.21



No.22



[0043] Among the above-mentioned organic phosphites, one having no cyclic structure containing a phosphorus atom, as expressed by the formula (1) is preferable, and a monophosphite is most preferable.

[0044] As amines, any one of primary, secondary and tertiary amines can be used, but a tertiary amine is particularly preferable. Particular examples include a substituted or unsubstituted pyridine, quinoline, isoquinoline, indole and phenanthroline, C₃-C₃₆ trialkylamines, and the like. Also, tertiary polyamines such as poly(2-propenylpyridine), poly(vinylpyridine), and the like can be used.

[0045] A concentration of a metal component in a reaction solution is determined depending on a kind of metal used, a reaction substrate and operation conditions of a reactor. For example, when a metal component is rhodium, a metal concentration is usually from 5 ppm to 500 ppm, preferably from 10 ppm to 300 ppm. When the metal component is cobalt, a metal concentration is usually from 50 ppm to 10,000 ppm, preferably from 100 ppm to 5,000 ppm. By feeding a catalyst component at an appropriate place other than an inlet of a continuous multistage reactor, it is possible to operate by varying a catalyst concentration in respective pressure sections.

[0046] In the present invention, the reaction may be carried out in the presence of an appropriate solvent if the presence of a solvent is favorable to the process, and also reaction substrates such as an unsaturated hydrocarbon, a product or a high boiling point material by-produced in the reaction system may be used as a solvent without adding a solvent. Such a solvent is preferably inert to the reaction, preferable examples of which include a saturated hydrocarbon compound such as hexane, heptane or the like, and an aromatic hydrocarbon such as toluene, xylene or the like. A

compound hardly separatable from a product or a substrate used is not preferable as a solvent to the process.

[0047] Also, the reaction can be carried out by adding an appropriate organic or inorganic additive if the addition of such an additive is favorable to the process.

5 EXAMPLES

[0048] The present invention is further illustrated with reference to Examples, but should not be limited to these Examples.

10 EXAMPLE 1

[0049] As illustrated in the attached Figure 1, a two stage continuous flow reactor having two stirring type autoclave reactors 5 and 9 connected in series was used for reaction. The upper parts of respective reactors had gas-supplying inlets 4 and 10, and the lower parts of the respective reactors had liquid-supplying inlets 3 and 8. A liquid-withdrawing outlet 6 of the reactor 5 and a liquid-withdrawing outlet 11 of the reactor 9 were respectively provided at such positions as to make a liquid phase volume ratio of the reactor 5 and the reactor 9 about 5:2, and a product was withdrawn by overflow from the liquid-withdrawing outlet 11 into a receiver 12.

[0050] A mixed octene/m-xylene/pyridine mixture solution (volume ratio 90/5/5) containing 125 mg/l of $\text{Rh}(\text{CO})_2(\text{acac})$ was charged into a starting material tank 1, and were continuously fed by means of liquid-feeding pumps 2 and 7 in such a manner as to make an average residence time (total) of the reaction solution in the two flow reactors about 7 hours. The reactors 5 and 9 were heated by heaters from outside, and respective liquid temperatures were controlled to 130°C, and a mixed gas of H_2/CO (ratio 1/1) was continuously supplied to respective reactors from the gas-supplying inlets 4 and 10 so as to make an internal pressure (total pressure of hydrogen and carbon monoxide) in the reactor 5 about 50 kg/cm² and an internal pressure (total pressure of hydrogen and carbon monoxide) in the reactor 9 about 170 kg/cm².

[0051] The composition of the mixed octene used herein was n-octenes 16%, 3-methylheptenes 66% and 3,4-dimethylhexenes 18%, and was obtained by dimerization of butene.

[0052] The reaction was continued until the composition of the liquid withdrawn from the liquid-withdrawing outlet 11 became substantially constant, and as this result, a conversion of the mixed octene was 92.2%, and a C9 alcohol/C9 aldehyde ratio in the product solution was 0.0896, and a selectivity of a terminal formylated product in (C9 alcohol + C9 aldehyde) was 42.8%.

[0053] The terminal formylated product selectivity is a ratio of a total amount of (1-nonanal, 6-methyloctanal, 4-methyloctanal, 4,5-dimethylheptanal, 1-nonanol, 6-methyloctanol, 4-methyloctanol and 4,5-dimethylheptanol) to the total amount of (C9 alcohol + C9 aldehyde).

[0054] The aldehyde product thus obtained is hydrogenated by a usual method using a catalyst such as nickel/diatomaceous earth, copper chromite or the like to obtain an alcohol suitable for use as a raw material of plasticizer, and the like.

COMPARATIVE EXAMPLE 1

[0055] The same procedure as in Example 1 was carried out, except that both internal pressures in the reactor 5 and in the reactor 9 were controlled to 170 kg/cm² and a total average residence time of the reaction solution was made 3 hours. As this result, a reaction conversion of mixed octene was 92.8%, and a C9 alcohol/C9 aldehyde ratio in the product solution was 0.0512, but a selectivity of a terminal formylated product was only 35.25%.

COMPARATIVE EXAMPLE 2

[0056] The same procedure as in Example 1 was carried out, except that both internal pressures in the reactor 5 and in the reactor 9 were controlled to 50 kg/cm². In order to make a conversion of mixed octene at least 90%, it was necessary to make a total average residence time in the reactors 5 and 9 a long time of about 20 hours, and it was proved that such a long residence time could not be employed for industrial practical use. After the average residence time of 20 hours, a reaction conversion was 90.4%, and a selectivity of a terminal formylated product was 42.6%, and after an average residence time of 26 hours, a reaction conversion was 93.5% and a conversion of a terminal formylated product was 42.2%.

[0057] By employing the process of the present invention, both of a high conversion of olefin and a high terminal formylation rate of a product can be achieved at the same time. Also, since it is possible to increase an amount of an alcohol product produced together with an aldehyde product, the present invention provides a great industrial merit of reducing a load of hydrogenation at a later step when the aldehyde product is used for preparing an alcohol for plasti-

cizer.

Claims

- 5 1. A process for preparing aldehydes which comprises reacting an olefinic unsaturated compound with hydrogen and carbon monoxide by hydroformylation reaction in the presence of a catalyst in a continuous multistage flow reactor, wherein the continuous multistage flow reactor contains n number ($n \geq 2$) of flow reactors, and the reaction is carried out in the presence of pressure sectional zones satisfying at least one of the following pressure conditions (1) to (3), provided that partial pressures of hydrogen and carbon monoxide in each reactor are illustrated as (10 $(P_{H_2(1)}, P_{CO(1)}), (P_{H_2(2)}, P_{CO(2)}), \dots (P_{H_2(n)}, P_{CO(n)})$) in order from the upper stream from the reactor,

$$P_{CO(m-1)} < P_{CO(m)} \quad (1)$$

$$P_{H_2(m-1)} < P_{H_2(m)} \quad (2)$$

$$P_{CO(m-1)} + P_{H_2(m-1)} < P_{CO(m)} + P_{H_2(m)} \quad (3)$$

in which m is an integer in the range of $2 \leq m \leq n$.

- 20 2. The process according to Claim 1, wherein the reaction is carried out in the presence of a pressure sectional zone satisfying at least the following pressure condition (1),

$$P_{CO(m-1)} < P_{CO(m)} \quad (1)$$

25 in which m is an integer in the range of $2 \leq m \leq n$.

3. The process according to Claim 1, wherein the reaction is carried out in the presence of a pressure sectional zone satisfying at least the following pressure condition (2),

$$P_{H_2(m-1)} < P_{H_2(m)} \quad (2)$$

in which m is an integer in the range of $2 \leq m \leq n$.

- 35 4. The process according to Claim 1, wherein the reaction is carried out in the presence of a pressure sectional zone satisfying at least the following pressure condition (3),

$$P_{CO(m-1)} + P_{H_2(m-1)} < P_{CO(m)} + P_{H_2(m)} \quad (3)$$

in which m is an integer in the range of $2 \leq m \leq n$.

- 40 5. The process according to any one of Claims 1 to 4, wherein the olefinic unsaturated compound is an internal olefin.

6. The process according to claim 5, wherein the internal olefin is one component of an octene mixture obtained by dimerization of butene.

- 45 7. The process according to any one of Claims 1 to 6, wherein the olefinic unsaturated compound is a C_3 - C_{12} unsaturated compound.

- 50 8. The process according to any one of Claims 1 to 4, wherein in is an integer of 2 in any one of the above formulae (1) to (3).

9. The process according to any one of Claims 1 to 8, wherein the reaction is carried out in a pressure sectional zone in which B/A is from 1.2 to 10, provided that among hydrogen partial pressures of n number of reactors, the lowest partial pressure value is A and the highest partial pressure value is B.

- 55 10. The process according to any one of Claims 1 to 9, wherein the reaction is carried out in a pressure sectional zone in which D/C is from 1.8 to 10, provided that among carbon monoxide partial pressures of n number of reactors, the lowest partial pressure value is C and the highest partial pressure value is D.

EP 1 008 580 A1

11. The process according to any one of Claims 1 to 10, wherein the reaction is carried out in a pressure sectional zone in which F/E is from 1.1 to 10, provided that among total partial pressures of hydrogen and carbon monoxide in n number of reactors, the lowest value is E and the highest value is F .

5 **12.** The process according to any one of Claims 1 to 11, wherein the number (n) of continuous flow reactors is from 2 to 5.

13. The process according to any one of Claims 1 to 12, wherein the catalyst contains an element of Groups 8 to 10 of the Periodic Table.

10

14. The process according to any one of Claims 1 to 13, wherein the catalyst contains a ligand selected from the group consisting of phosphines, phosphites and amines.

10

15 **15.** The process according to any one of Claims 1 to 14, wherein a reaction conversion of the olefinic unsaturated compound is from 75 to 100%.

16. A process for preparing alcohols, which comprises preparing aldehydes by any one of the methods according to any one of Claims 1 to 15 and then hydrogenating the aldehydes thus prepared.

20

25

30

35

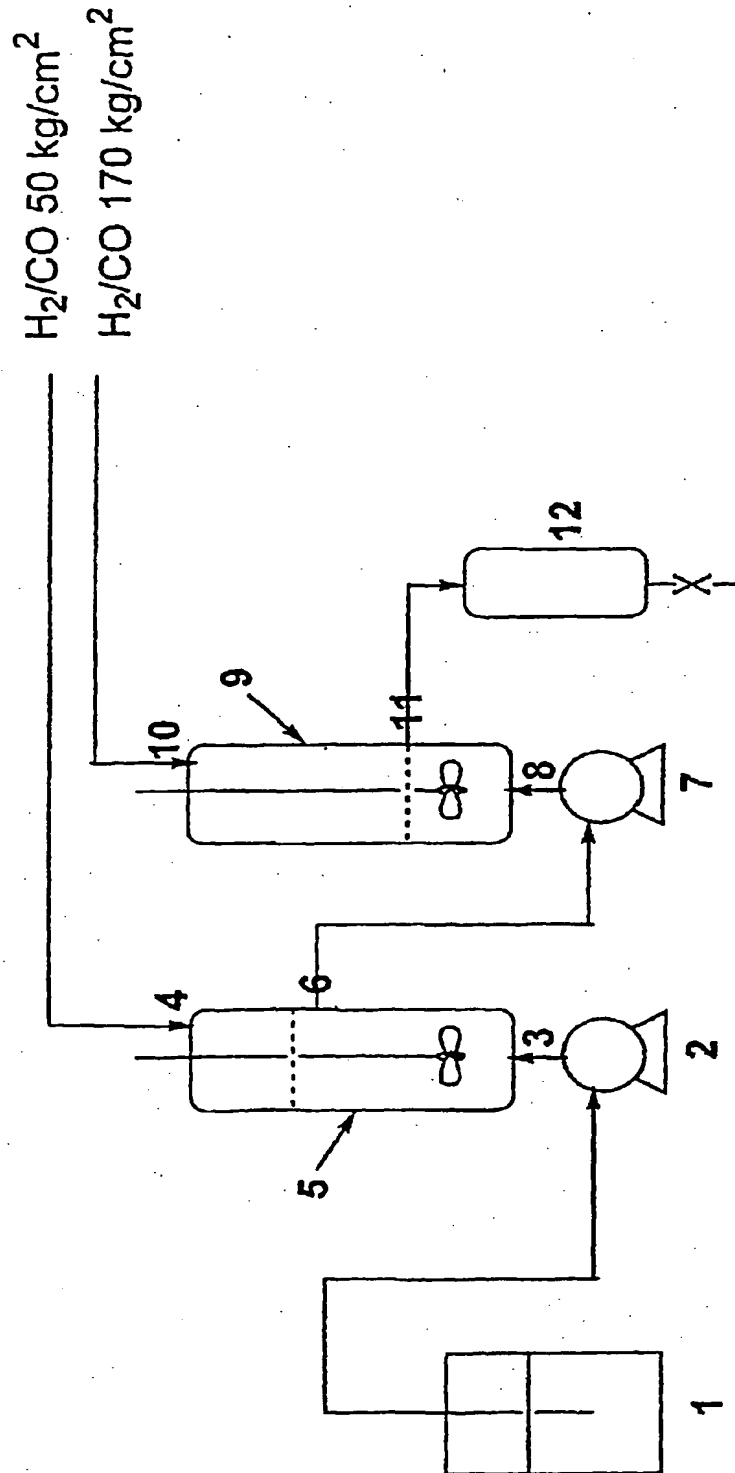
40

45

50

55

FIG. 1





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 12 4566

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 4 533 755 A (CORNILS BOY ET AL) 6 August 1985 (1985-08-06) * the whole document *	1,7,13,14	C07C45/50 C07C29/141
A	US 5 189 105 A (MIYAZAWA CHIHIRO ET AL) 23 February 1993 (1993-02-23) * example 1 *	6,16	
A	US 5 808 168 A (ZGORZELSKI WOLFGANG ET AL) 15 September 1998 (1998-09-15) * claims *	1	
A	US 4 716 250 A (BRYANT DAVID R ET AL) 29 December 1987 (1987-12-29) * example 9 *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C07C
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		14 February 2000	Bonnevalle, E
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.92 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 12 4566

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-02-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4533755 A	06-08-1985	DE 3245883 A	14-06-1984
		AT 12764 T	15-05-1985
		AU 560214 B	02-04-1987
		AU 2227683 A	14-06-1984
		CS 8309042 A	13-06-1985
		EP 0111257 A	20-06-1984
		JP 1616897 C	30-08-1991
		JP 2036579 B	17-08-1990
		JP 59110642 A	26-06-1984
US 5189105 A	23-02-1993	US 5468419 A	21-11-1995
		DE 3889936 D	14-07-1994
		DE 3889936 T	26-01-1995
		EP 0278407 A	17-08-1988
		JP 1779879 C	13-08-1993
		JP 4038735 B	25-06-1992
		JP 64000037 A	05-01-1989
		KR 9603825 B	22-03-1996
US 5808168 A	15-09-1998	DE 19617257 A	06-11-1997
		AU 709597 B	02-09-1999
		AU 1908297 A	06-11-1997
		CA 2203311 A	30-10-1997
		CN 1168877 A	31-12-1997
		EP 0805138 A	05-11-1997
		JP 2984231 B	29-11-1999
		JP 10053551 A	24-02-1998
		PL 319622 A	10-11-1997
US 4716250 A	29-12-1987	AT 74120 T	15-04-1992
		AU 605773 B	24-01-1991
		AU 7553187 A	14-01-1988
		BE 1001190 A	16-08-1989
		BR 8703510 A	22-03-1988
		CA 1307006 A	01-09-1992
		CN 1020720 B	19-05-1993
		CS 8705276 A	12-02-1990
		DE 3722928 A	21-01-1988
		DE 3777714 A	30-04-1992
		DK 359987 A	11-01-1988
		EP 0254937 A	03-02-1988
		ES 2007367 A	16-06-1989
		FI 873054 A,B,	11-01-1988
		FR 2603579 A	11-03-1988
		GB 2193494 A,B	10-02-1988
		HU 48193 A,B	29-05-1989

EPO FORM P/459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 12 4566

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-02-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4716250 A		IN 169702 A	14-12-1991
		IT 1221979 B	31-08-1990
		JP 1836011 C	11-04-1994
		JP 5048214 B	20-07-1993
		JP 63088150 A	19-04-1988
		KR 9108369 B	12-10-1991
		MX 166891 B	11-02-1993
		NL 8701626 A	01-02-1988
		NO 872887 A, B,	11-01-1988
		SE 8702822 A	11-01-1988
		SU 1715202 A	23-02-1992
		YU 129787 A	30-04-1988
		ZA 8705058 A	30-03-1988
